

# THERMODYNAMIC PROPERTIES OF INDANE AND INDENE

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## INTRODUCTION

Over a score of years ago, Dolliver, Gresham, Kistiakowsky and Vaughan<sup>1</sup> measured the heat of catalysed hydrogenation at 100°C of indane and indene to the same hydrogenated product, which was presumed to be a mixture of isomers whose identity and concentration were not definitely established. The difference between these measured heat values is a measure of the heat of hydrogenation of indene to indane. More recently Naidus and Mueller<sup>2</sup> measured the equilibrium constants by a flow method for the system indane-indene-hydrogen from 375° to 535°C. From these equilibrium data these authors calculated the heat, entropy, and free energy changes for the hydrogenation reaction over the temperature range studied. Since the industrial importance of these materials has increased in the past few years, the following measurements were undertaken to extend our knowledge in this area. The heat capacities of indane and indene were measured from 15° to 320°K, and their heats of combustion were determined by standard bomb calorimetry.

## EXPERIMENTAL

### Materials

*Indane*—Commercial material was purchased from the Aldrich Chemical Company, Milwaukee, Wisconsin, and was further purified by distillation. The equilibrium melting studies indicated the indane to be 99.89 mole per cent pure. The calorimetric sample weighed 62.245 g corrected to a vacuum basis and the molecular weight was taken as 118.179.

*Indene*—Commercial material was purchased from the Chemical Research and Intermediates Laboratories, Akron, Ohio, and was further purified by distillation. The equilibrium melting studies indicate purity in the range 99.7 to 99.9 mole per cent, although this has not been clearly established because of solid solution phenomena. The calorimetric sample weighed 63.900 g corrected to a vacuum basis and the molecular weight used was 116.163.

### Calorimetric apparatus

Details of the automatic adiabatic calorimeter and its operation have been fully presented elsewhere<sup>3, 4</sup>. The sample container was of platinum,

joined with gold solder and contained a soft-glass cap which was sealed off to close the container hermetically. The container had a volume of about 70 cm<sup>3</sup> and contained a central platinum resistance thermometer with ten re-entrant heater wells about midway on equidistant radii. Twenty circular heat-distributing discs were bonded to the heaters but not to the resistance thermometer or side. For filling, the container was sealed to a glass vacuum line. After evacuation the sample was distilled in under its own vapour pressure, and the glass filling line sealed off after addition of a few cubic centimetres of helium gas. The quantity of glass used was weighed and corrected for.

The platinum resistance thermometer ( $R_0 = 92 \Omega$ ) was calibrated by comparison with another platinum resistance thermometer calibrated by the National Bureau of Standards, and thus reproduced the temperature scale described by Hoge and Brickwedde<sup>5</sup> and by Stimson<sup>6</sup>. The value 273.15°K was used for the ice point and 4.1840 abs. J has been used to define the calorie.

### Heat capacity measurements

Comparison of heat capacity measurements on n-heptane<sup>4</sup> with the standard values reported by Ginnings and Furukawa<sup>7</sup> has shown that this automatic adiabatic calorimeter is accurate to within 0.25 per cent above 50°K, while below this temperature the uncertainty increases to as much as 1 per cent at 25°K. Additional comparisons of heat capacity values with other laboratories are in agreement with these findings.

Indane was cooled to about 12°K after which intermittent quantities of heat were added, finally raising the temperature to about 300°K. A sharp peak was observed in the heat capacity at about 70°K and fusion at about 222°K. After re-cooling to about 12°K, intermittent heating raised the temperature to about 70°K where the transition was again passed. After re-cooling some degrees below the transition, heat inputs were resumed with smaller increments through the transition range. After re-cooling a second time to below the 70°K transition, intermittent heat inputs were made until the temperature of the sample reached about 320°K. The fusion was carried out twice with continuous heating, after which the liquid range was measured to 310°K. Temperature rises were about 10 per cent of the absolute temperature below 50°K and 5° to 6° above, and were small enough so that curvature corrections were unnecessary.

Indene was cooled to about 12°K and was heated to about 290°K with intermittent heat inputs. After re-cooling to about 12°K intermittent heat inputs were made until 320°K was reached while the fusion was carried out with continuous heating. After re-solidification, the fusion was again accomplished with continuous heating. Indene has an abrupt rise in its heat capacity at about 125°K, similar to an annealing type of transition encountered with organic glasses, and in addition, a rather broad hump at about 210° to 250°K. *Table 1* lists thermal data derived from the smoothed heat capacity data on indane and indene read from smoothed curves drawn through the experimental points. Few of the experimental points were more than 0.2 per cent from the "best curve".

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Table 1. Derived thermal data

$T^{\circ}(\text{K})$	$C_p^{\circ}$	$S^{\circ}$ (cal mole <sup>-1</sup> K <sup>-1</sup> )	$\frac{H^{\circ}-H_0^{\circ}}{T}$	$-\frac{F^{\circ}-H_0^{\circ}}{T}$
<i>Indane</i>				
15	1.86	0.72	0.53	0.19
20	3.24	1.45	1.03	0.41
25	4.68	2.32	1.62	0.71
30	6.03	3.30	2.24	1.06
40	8.30	5.35	3.48	1.87
50	10.28	7.42	4.64	2.78
60	12.26	9.47	5.75	3.72
80	14.43	14.04	8.15	5.89
100	16.10	17.43	9.57	7.86
120	17.84	20.52	10.80	9.72
140	19.68	23.40	11.97	11.42
160	21.66	26.16	13.06	13.10
180	23.79	28.84	14.13	14.70
200	26.04	31.46	15.21	16.25
220	28.43	34.05	16.30	17.75
240	40.70	46.71	26.76	19.95
260	42.14	50.03	27.89	22.14
280	43.80	53.21	28.96	24.24
298.15	45.47	56.01	29.92	26.09
300	45.65	56.29	30.01	26.28
320	47.79	59.31	31.06	28.25
<i>Indene</i>				
15	2.13	0.91	0.66	0.26
20	3.42	1.71	1.19	0.51
25	4.66	2.60	1.76	0.84
30	5.77	3.55	2.34	1.21
40	7.64	5.48	3.44	2.04
50	9.09	7.35	4.43	2.92
60	10.35	9.12	5.32	3.80
80	12.48	12.40	6.72	5.67
100	14.22	15.38	8.05	7.32
120	16.02	18.12	9.22	8.89
140	19.35	20.86	10.45	10.41
160	21.54	23.56	11.70	11.85
180	23.64	26.22	12.91	13.30
200	25.81	28.82	14.09	14.09
220	28.56	31.40	15.28	16.12
240	31.42	34.01	16.50	17.51
260	34.02	36.62	17.74	18.88
280	43.25	48.43	27.92	20.51
298.15	44.68	51.19	28.89	22.30
300	44.84	51.47	28.99	22.48
320	46.54	54.21	30.06	24.14

## RESULTS

## Transition data

The heat capacity of indane begins to rise sharply at about 68°K and reaches a measured value of 138.88 cal mole<sup>-1</sup> °K<sup>-1</sup> at 73.82°K; the value at 74.28°K has receded to 33.21 cal mole<sup>-1</sup> °K<sup>-1</sup>. By 78°K the heat capacity curve is rising smoothly again. Two separate runs through the transition region gave for the total heat absorbed between 68° and 78°K the values 187.0 and 186.1 cal/mole, indicating that the transition is reasonably reversible and free from hysteresis. Pre-melting seems to begin about 170°K and 180°K and becomes more pronounced as the melting point is approached. The heat of melting in the pre-melting region is about 0.3 to 0.5 per cent. The heats of melting for the four runs were 2054.8, 2056.0, 2054.8 and 2055.0, making the average value 2055 ± 2 cal/mole. Purity of the sample was calculated from melting data taken during intermittent melting, and tabulated in *Table 2* where *F* is the weight fraction melted. Our sample melted at 221.715°K, extrapolated to a pure melting point of 221.77°K, and gave a calculated purity of 99.89 mole per cent. The sample appears to behave ideally.

The shape of the solid heat capacity curve of indene does not give much of a clue regarding the presence or absence of pre-melting. The heats of melting for three runs were 2440.3, 2435.9, and 2437.7, making the average value 2438 ± 3 cal/mole. Purity calculated on the basis of the pre-melting heat capacity indicates about 99.95 mole per cent. Purity calculated from fractional melting data is tabulated in *Table 3* and indicates a purity of about 99.91 mole per cent although a plot of temperature *versus* the reciprocal of the fraction melted does not give a straight line, indicating that the

*Table 2.* Equilibrium fraction of indane melted (*F*) *vs.* temperature

<i>T</i> °(K)	<i>F</i>	1/ <i>F</i>
221.438	0.129	7.74
221.570	0.238	4.20
221.616	0.351	2.85
221.651	0.463	2.16
221.673	0.575	1.74
221.687	0.690	1.45
221.703	0.800	1.25
221.714	0.909	1.10

*Table 3.* Equilibrium fraction of indene melted (*F*) *vs.* temperature

<i>T</i> °(K)	<i>F</i>	1/ <i>F</i>
271.508	0.294	3.40
271.541	0.413	2.42
271.565	0.532	1.88
271.582	0.654	1.53
271.598	0.775	1.29
271.614	0.893	1.12

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system departs rather widely from ideality. If the impurity forms a solid solution, application of the calculational method of Mastrangelo and Dornte<sup>8</sup> leads to a purity of 99.68 mole per cent. No one of these treatments is in agreement with all the facts, so the purity must be regarded as not established. The melting point of pure indene was taken as 271.70°K.

## Entropy

Both heat capacity curves were extrapolated from about 15°K to 0°K by a combination of Einstein and Debye functions. For indane three degrees of Debye freedom with  $\theta = 86^\circ$  and three degrees of Einstein freedom with  $\theta = 121^\circ$  were used, while for indene three degrees of Debye freedom with  $\theta = 77.5^\circ$  and three degrees of Einstein freedom with  $\theta = 136^\circ$ . From 15°K to 198.15°K the heat capacity was graphically integrated. These entropy calculations are summarized in *Tables 4* and *5*.

Table 4. Calorimetric entropy of indane

	$S^\circ$ (cal mole <sup>-1</sup> K <sup>-1</sup> )
0°K-15°K $\left[ C_v = 3^\circ D \left( \frac{86}{T} \right) + 3^\circ E \left( \frac{121}{T} \right) \right]$	0.724
15°K-221.77°K (graphical)	33.555
Melting, 2055/221.77	9.266
221.77°K-298.15°K (graphical)	12.464
Entropy of liquid indane at 298.15°K	56.01 ± 0.10

Table 5. Calorimetric entropy of indene

	$S^\circ$ (cal mole <sup>-1</sup> K <sup>-1</sup> )
0°K-15°K $\left[ C_v = 3^\circ D \left( \frac{77.5}{T} \right) + 3^\circ E \left( \frac{136}{T} \right) \right]$	0.912
15°K-271.70°K (graphical)	37.251
Melting, 2438/271.70	8.973
271.70°K-298.15°K (graphical)	4.053
Entropy of liquid indene at 298.15°K	51.19 ± 0.10

## Vapour pressure

Vapour pressures were measured in a twin ebulliometer system in which the compounds and water boiled simultaneously at a common pressure. Equilibrium boiling temperatures were observed simultaneously for water and indane and for water and indene. The pressure in the system was calculated from the boiling temperature of the water, since the vapour pressure of water is well established. The experimental points were fitted by a least-squares method to the Antoine equation. The Antoine equation for indane:  $\log P_{\text{mm}} = 7.05483 - 1625.70/(t + 211.645)$ , and for indene:  $\log P_{\text{mm}} = 6.87071 - 1507.80/(t + 195.313)$ , ( $t$  in °C), were used to calculate the vapour pressure values presented in *Table 6*.

Table 6. Vapour pressures of indane and indene

Indane pressures (mm)			
$t(^{\circ}\text{C})$	Obs.	Calc.	(Calc.—Obs.)
179.09	783.38	783.72	+ 0.34
178.04	763.03	763.75	+ 0.72
176.03	727.55	726.62	- 0.93
152.36	388.28	387.82	- 0.46
128.56	189.10	188.88	- 0.22
107.38	90.65	90.97	+ 0.32
91.68	49.68	49.56	- 0.12
Indene pressures (mm)			
183.82	783.11	782.90	- 0.21
182.72	763.03	762.32	- 0.71
180.79	727.81	727.23	- 0.58
156.95	387.81	389.36	+ 1.55
132.89	189.36	189.04	- 0.32
111.48	90.60	90.35	- 0.25
96.06	49.60	49.68	+ 0.08

### Heats of combustion

Heats of combustion of the low-temperature samples were determined by standard bomb calorimetry<sup>9</sup>. The combustion calorimeter was calibrated with N.B.S. benzoic acid. Samples were enclosed in "Mylar" film to prevent evaporation and exposure to oxygen. All weights were corrected to true mass (weight in vacuum). Corrections to standard states of pure liquids and gases at one atmosphere were calculated by the method of Prosen<sup>10</sup>. Results are for 298.15°K and a constant pressure of one atmosphere. The heat of combustion refers to the reaction with oxygen to form liquid water ( $\Delta H_{\text{f}}^{\circ}, 298^{\circ}\text{K} = -68.317$  kcal/mole), and gaseous carbon dioxide ( $\Delta H_{\text{f}}^{\circ}, 298^{\circ}\text{K} = -94.054$  kcal/mole). The heat of formation refers to the reaction of graphite and hydrogen to form liquid indane or indene. Atomic weights used were C = 12.011 and H = 1.0080. The values given in Table 7 are the averages of five combustions on each material.

Uncertainties are equal to twice the overall standard deviation.

Table 7. Heat of combustion and formation of indane and indene at 298.15°K

	$\Delta H_{\text{c}}$ (kcal/mole)	$\Delta H_{\text{f}}$ (kcal/mole)
Indane (liquid)	- 1190.63 $\pm$ 0.47	+ 2.56 $\pm$ 0.47
Indene (liquid)	- 1146.15 $\pm$ 0.30	+ 26.39 $\pm$ 0.30

The difference between the values in the third column of Table 7 represents the heat of hydrogenation of liquid indene to form liquid indane, which is  $-23,830 \pm 770$  cal/mole. Dolliver, Gresham, Kistiakowsky, and

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Vaughan<sup>1</sup> measured the heat of hydrogenation of indene to indane in the gas phase at 373°K, and reported  $-24,200 \pm 500$  cal/mole. Since the heats of vaporization for indane and indene are expected to be similar, these heats of hydrogenation are in agreement within experimental error.

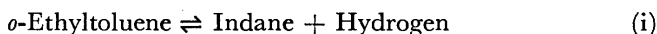
**Thermodynamic properties at 298·15°K**

The entropy and heat of formation data given above may be combined with the entropies of the elements<sup>11</sup> to calculate free energies of formation of indane and indene. Thermodynamic properties of *o*-ethyltoluene were taken from the compilation of the American Petroleum Institute Research Project 44<sup>12</sup>. These thermodynamic properties are summarized in *Table 8*.

*Table 8.* Thermodynamic properties at 298·15°K

	$\Delta F_f^\circ$ (kcal/mole)	$\Delta H_f^\circ$ (kcal/mole)	$S^\circ$ (cal mole <sup>-1</sup> °K <sup>-1</sup> )
<i>o</i> -Ethyltoluene (liq.)	27·97	- 11·11	68·42
Indane (liq.)	36·06	2·56	56·01
Indene (liq.)	52·02	26·39	51·19
Hydrogen (gas)	0	0	31·21

On the basis of these data, the extent of two reactions at thermodynamic equilibrium has been calculated.



Reaction (i) indicates the cracking of liquid *o*-ethyltoluene at 25°C to form liquid indane and hydrogen gas:

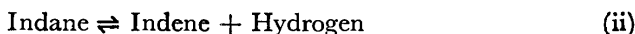
$$\Delta F_{R, 25^\circ\text{C}} = 36\cdot06 - 27\cdot97 = + 8\cdot09 \text{ kcal}$$

$$\Delta H_{R, 25^\circ\text{C}} = 2\cdot56 - (- 11\cdot11) = + 13\cdot67 \text{ kcal}$$

$$\Delta S_{R, 25^\circ\text{C}} = 56\cdot01 + 31\cdot21 - 68\cdot42 = 18\cdot80 \text{ cal/}^\circ\text{K}$$

The free energy change indicates that no indane would be formed at room temperature, but the large positive entropy change indicates that indane formation would be favoured at higher temperatures. Assuming that the heat and entropy changes in the reaction remain reasonably constant with temperature and that the heats of vaporization at 25°C are comparable, calculation shows that the free energy change for the reaction,  $\Delta F_R$ , should be equal to zero at about 750°K (480°C). This means that roughly equal amounts of *o*-ethyltoluene and indane would be present at that temperature, and that above 750°K the formation of indane becomes increasingly favoured. Experience has shown that the assumptions regarding the constancy of  $\Delta H$  and  $\Delta S$  are reasonable.

For the reaction of dehydrogenating liquid indane to indene liquid and gaseous hydrogen:



$$\Delta F_{R, 25^\circ\text{C}} = 52\cdot02 - 36\cdot06 = + 15\cdot96 \text{ kcal}$$

$$\Delta H_{R, 25^\circ\text{C}} = 26\cdot39 - 2\cdot56 = + 23\cdot83 \text{ kcal}$$

$$\Delta S_{R, 25^\circ\text{C}} = 51\cdot19 + 31\cdot21 - 56\cdot01 = + 26\cdot39 \text{ cal/}^\circ\text{K}$$

Here, also, the free energy change indicates that the dehydrogenation of indane to indene does not occur to any measurable extent at room temperature. Again, however, the large positive entropy change indicates that indene formation should be favoured at higher temperatures. Making the same assumptions regarding the constancy of  $\Delta H$  and  $\Delta S$  and again assuming the heats of vaporization to be comparable, the free energy change in reaction (ii) should be zero at about 900°K (630°C). In the temperature range 600°C to 750°C, these results indicate that roughly equal amounts of indane and indene may be present around 600°C, but at 750°C indene should be favoured over indane by a ratio of almost ten to one.

Naidus and Mueller<sup>2</sup> have presented an experimental study of the indene-indane-hydrogen system from 375°C to 525°C. Their results are in reasonably good agreement with these thermodynamic calculations, but indicate that  $\Delta F$  for reaction (ii) should be equal to zero at about 530°C, about 100° lower than our calculated value. Considering the errors involved, we are inclined to average the two sets of results and conclude that indane and indene will be present in roughly equal amounts at about 580°C. Above this temperature, of course, indene predominates.

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